

Supporting information for

**Bi-functional Mechanism of CH₄ Dry Reforming over a
Ni-CaO-ZrO₂ Catalyst: Further Evidence via Active Sites**

Identification and Kinetic Studies

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SI 1 Ni-carbon compound diffractions on similar Ni-CaO-ZrO₂ catalysts with different SMSI effect.

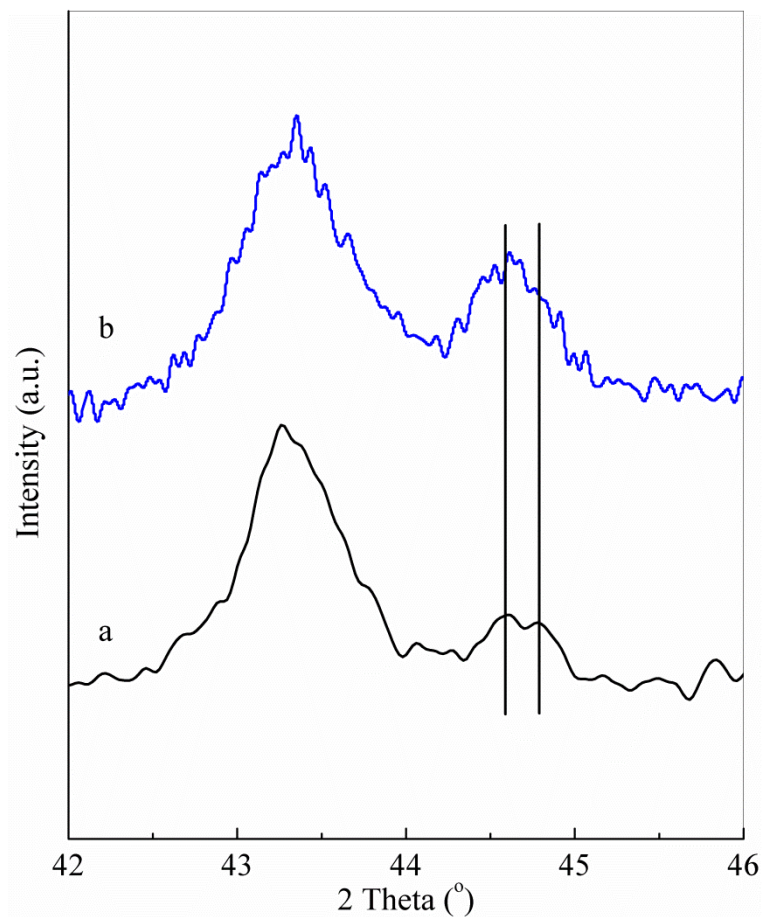


Fig. S1. Fine scanning XRD patterns of spent Ni-CaO-ZrO₂ catalyst prepared with different method at 42-46°.

a) Ni-CaO-ZrO₂ with fine SMSI effect, b) Ni-CaO-ZrO₂ with less SMSI effect.

Fig. S1 shows that the diffraction of the non-stoichiometric Ni-carbon compound cannot be clearly distinguished in a Ni-CaO-ZrO₂ catalyst with less SMSI.

SI2 Stability test

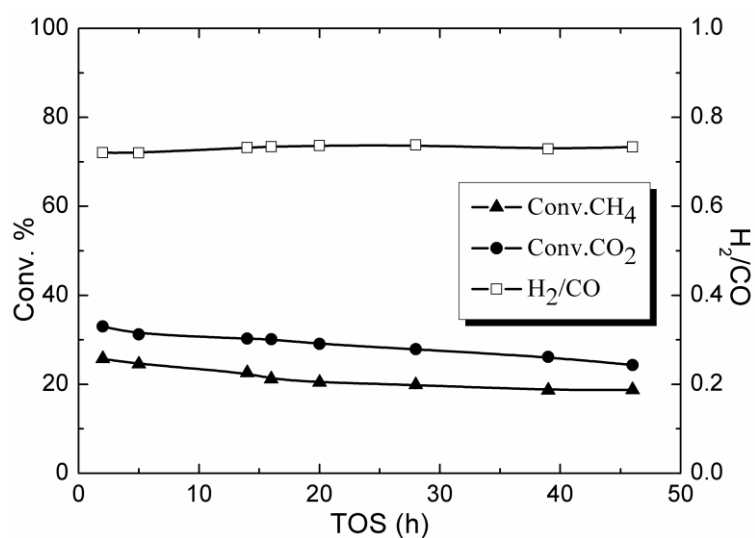


Fig. S2. Stability test under differential condition
(750 °C, P_{CO₂}:P_{CH₄}: P_{Ar} =1:1:1, GHSV=1200 L g⁻¹ h⁻¹)

Fig. S2 shows the CH₄ and CO₂ conversions versus time on stream under *differential* conditions. They are significantly lower than thermodynamic equilibrium values due to shorter contact time. The conversion of CH₄ and CO₂ decreased slightly in the first four hours and remain stable for 45 h. Consequently, the kinetic data were taken after the reaction proceeds for at least 4 h to ensure stable performance of the catalyst.

S13 Mass transport effects

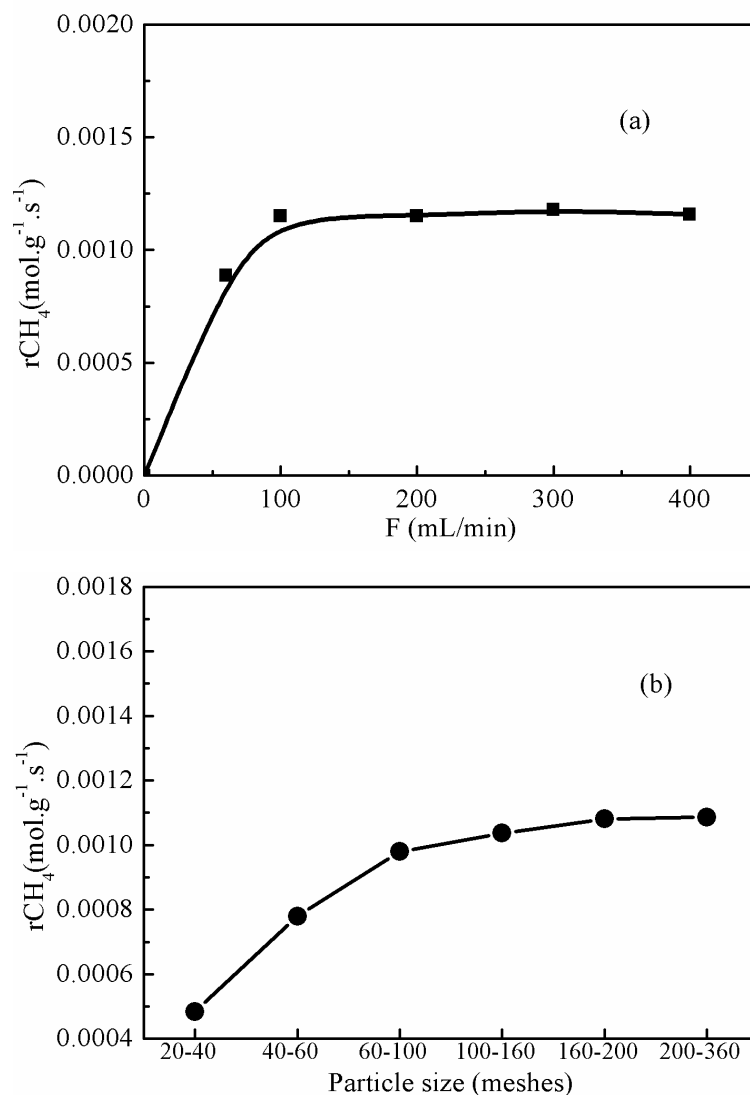


Figure S3. Determination of kinetic regime

(a) Effect of feed flow rate at constant W/F (0.003 g s mL⁻¹)

(b) Effect of particle size at constant W/F ratio (0.003 g s mL⁻¹)

The effect of external mass transfer limitation was studied experimentally with a fixed residence time through a variation of feed velocity, and possible effect of internal diffusion limitation was investigated by carrying out the reactions with a flow rate of 300 mL/min under a constant W/F ratio (0.003 g s mL⁻¹) using catalyst particles of diameters from 20 to 300 meshes. The results showed in Fig. S3 suggests that the kinetic data was collected without any diffusion influence.

SI4 Parity chart and optimized kinetic parameters

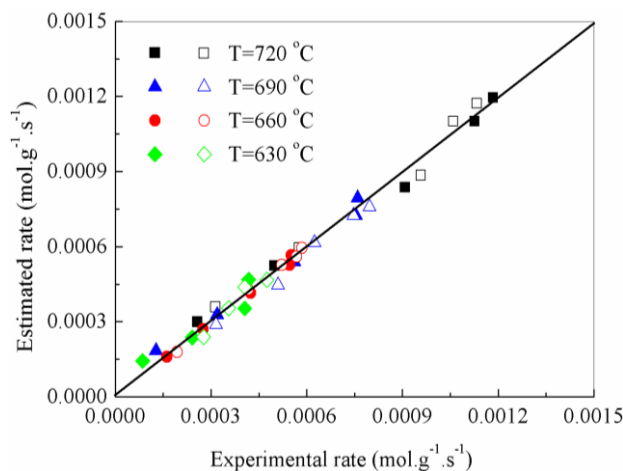


Fig. S4. Parity chart comparing between predicted and measured reaction rate

The simulation and experimental results are given in the parity chart (Fig. S4), which compares the experimental conversions of methane with those predicted by solving the kinetic model Eqn. (10). It shows a very good correlation between the calculated and experimental reaction rates obtained at different temperatures.

In Eqn. (10), K_{CH_4} is the equilibrium constant of methane adsorption and k_{CH_4} is the rate constant of the methane cracking. The two constants could not be determined individually but if we considered the methane adsorption and cracking together, we could get a simple parameter k'_{CH_4} , where $k'_{\text{CH}_4} = K_{\text{CH}_4} k_{\text{CH}_4}$ (11), and might represent the apparent rate constant of the decomposition of methane on the metal.

The optimized kinetic parameters determined with this model were provided in Table 3. The parameters in Table 3 were related at all temperatures by the Arrhenius and van't Hoff equations, so the rate constants of Eqn. 8 and 11 and equilibrium constant of Eqn. (7) have the following forms for the Ni-CaO-ZrO₂ catalyst system:

$$k = 1.57 \times 10^5 \times \exp(-14720.9/T) [\text{mol g}^{-1} \text{s}^{-1}] \quad (12)$$

$$k'_{\text{CH}_4} = 1.01 \times \exp(-9217.5/T) [\text{mol g}^{-1} \text{s}^{-1} \text{kPa}^{-1}] \quad (13)$$

$$K_{\text{CO}_2} = 2.73 \times 10^{-6} \times \exp(8161.4/T) [\text{kPa}^{-1}] \quad (14)$$